2001 ANNUAL DATA QUALITY REPORT

AIR RESOURCES BOARD MONITORING AND LABORATORY DIVISION

2001

Annual Data Quality Report

for the

Monitoring and Laboratory Division's and Local Districts' Air Monitoring Networks

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I. INTRODUCTION

The purpose of this report is to provide ambient air quality data users with a summary of the quality of the 2001 ambient data in quantifiable terms. This is the fourth edition of the report and presents an overview of various quality assurance and quality control activities. The tables included in this report provide summary data for ambient air monitoring stations in the statewide network.

The California Air Resources Board's (ARB) mission is to promote and protect public health, welfare, and ecological resources through effective and efficient reduction of air pollutants while recognizing and considering the effects on the economy of the State. The Monitoring and Laboratory Division (MLD) provides a key element of that mission through collecting and reporting on quality information on a large number of pollutants and for a vast air monitoring network. The MLD, directed by State law, conducts ambient air monitoring in support of ARB, local air pollution control and air quality management districts (districts), and the United States Environmental Protection Agency (U.S. EPA). Monitoring programs include gaseous criteria and non-criteria pollutants, particulate matter, toxic air contaminants, non-methane hydrocarbons, pesticides, consumer products, meteorological parameters, asbestos, and visibility. Data from these monitoring sources provide the means to determine the nature of the pollution problem and assess the effectiveness of the control measures and programs. The MLD mission includes supporting the regulatory and assessment programs of the Board.

It is the goal of MLD to provide accurate, relevant, and timely measurements of air pollutants and their precursors to support California's Air Quality Management Program for the protection of public health. The Quality Assurance Section (QAS) conducts various quality assurance activities to ensure that data collected comply with procedures and regulations set forth by the U.S. EPA and can be considered good quality data and data-for-record.

What is quality assurance? Quality assurance is an integrated system of management activities that involves planning, implementing, assessing, and assuring data quality through a process, item, or service that meets users needs for quality, completeness, representativeness and usefulness. Known data quality enables users to make judgements about compliance with air quality standards, air quality trends and health effects based on sound data with a known level of confidence. The objective of quality assurance is to provide



accurate and precise data, minimize data loss due to malfunctions, and to assess the validity of the air monitoring data to provide representative and comparable data of known precision and accuracy.

Quality assurance is composed of two activities: quality control and quality assessment. *Quality control* is composed of a set of internal tasks performed routinely at the instrument level that ensures accurate and precise measured ambient air quality data. *Quality control* tasks address sample collection, handling, analysis, and reporting. Examples include calibrations, routine service checks, chain-of-custody documentation,

duplicate analyses, development and maintenance of standard operating procedures, and routine preparation of quality control reports.

Quality assessment is a set of external, quantitative tasks that provide certainty that the quality control system is satisfactory and that the stated quantitative programmatic objectives for air quality data are indeed met. Staff independent of data generators performs these external tasks. Tasks include conducting regular performance audits, on-site system audits, interlaboratory comparisons, and periodic evaluations of internal quality control data. Table 1 illustrates the types of performance audits currently performed by the ARB for each air monitoring program. Field and laboratory performance audits are the most common. System audits are performed on an as-need basis or by request. Whole air sample comparisons are conducted for the toxic air contaminants and non-methane hydrocarbon programs.

Table 1. Audits Performed for Each Air Monitoring Program in 2001

Air Monitoring Program	Field Performance Audit	Laboratory Performance Audit	System Audit	Whole Air Audit
Gaseous Pollutants	X	Х	Future	
Particulate Matter	X	X	Χ	
Toxic Air Contaminants	X	X		X
Non-Methane Hydrocarbons	X	X	Χ	X
Pesticides	X			
Consumer Products		X		
Meteorology	X		Future	

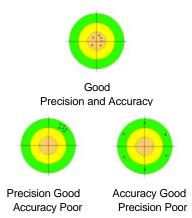
II. QUALITY CONTROL AND QUALITY ASSESSMENT

The QAS supports all ambient monitoring programs undertaken by MLD, which in 2001 includes gaseous pollutants, particulate pollutants, toxic air contaminants, non-methane hydrocarbons, pesticides, consumer products, and meteorologic sensors run by the ARB and local and private air monitoring agencies. There are approximately 230 air monitoring sites in 14 separate air basins operating in California.

Appendix A provides information about the air monitoring network (i.e., sampling schedules, number of instruments, collection/analysis method, etc.). The information in Appendix A is also available at the following Internet site under Air Monitoring Activities at http://www.arb.ca.gov/aaqm/qmosqual/qmosqual.htm.

Information about each air monitoring station audited by the ARB is available at http://www.arb.ca.gov/qaweb/. The web site includes maps of each site, latitude and longitude coordinates as determined by GPS, site photos, precision and accuracy data, and a detailed survey of the physical parameters and conditions at each site. The site surveys list in-depth monitoring information such as traffic descriptions, calibration dates, distances to trees and obstacles, and residence times. This site also includes an area for District precision and accuracy reports. These reports are available on a limited basis to District staff.

The air quality monitors collect data in both real-time and on a time integrated basis. The data are used to define the nature, extent, and trends of air quality in the State; to support programs required by State and federal laws; and to track progress in attaining air quality The precision and accuracy necessary depends on how the data will be used. The illustration to the right shows the relationship between precision and accuracy. From the figure, it is evident how important having good precision and accuracy is to ensuring good data quality. Data that must meet specific requirements (i.e., criteria pollutants) are referred to as controlled data sets. Criteria for the accuracy, precision, completeness, and sensitivity of the measurement in controlled data sets must be met and documented.



Air Quality Data Actions (AQDAs) are a key tool used by the QAS to confirm the data set meets the established control limits. They are initiated generally by auditors upon a failed audit and resolved after a review of calibrations, precision checks, and audit results. The AQDA must confirm that an analyzer/sampler has operated within ARB's control limits of +/-15% (+/-10% for PM10 and +/-4% for PM2.5), or for siting or temperature conditions otherwise, further action is taken.

Data without formal data quality objectives (i.e., toxics) are called *descriptive data sets*. The data quality measurements are made as accurately as possible in consideration of how the data are being used. Quantified quality assessment results describe the measurement variability in standard terminology, but no effort is made to confine the data set to values within a predetermined quality limit.

The ARB's Quality Assurance Program is outlined in a six-volume *Quality Assurance Manual*. The volumes, listed below, guide the operation of the quality assurance programs used by the ARB, local districts, and private industry in California.

Volume I	Quality Assurance Plan
Volume II	Standard Operating Procedures for Air Quality Monitoring
Volume III	Laboratory Standard Operating Procedures
Volume IV	Monitoring Methods for the State Ambient Air Quality Standards
Volume V	Audit Procedures for Air Quality Monitoring
Volume VI	Standard Operating Procedures for Stationary Source
	Emission Monitoring and Testing

The six-volume Quality Assurance Manual is available on the internet at http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm. Volume I lists the data quality objectives and describes quality control and quality assessment activities used to ensure that the data quality objectives are met.

A. Gaseous Pollutants

Ambient concentrations of carbon monoxide (CO), nitrogen dioxide (NO2), ozone (O3), sulfur dioxide (SO2), and hydrogen sulfide (H2S) are continuously monitored by an automated network of stations run by MLD and the districts. Non-criteria pollutants such as methane (CH4) and total hydrocarbons (THC) are also monitored continuously as precursors for criteria pollutants to help ensure the ambient air quality standards are met. Exposure to these pollutants cause adverse health effects which include respiratory impairment, fatigue, permanent lung damage, and increased susceptibility to infection in the general population. Gaseous criteria and non-criteria pollutant data are a controlled data set and are subject to meeting mandatory regulations.



Sampling Cane

<u>Accuracy (field)</u>: Annually, the QAS conducts field through-the-probe (TTP) performance audits for gaseous pollutants (criteria and non-criteria) to verify the system accuracy of the automated methods and to ensure the integrity of the sampling system.

Accuracy is represented as an average percent difference. The average percent difference is the combined differences from the certified value of all the individual audit points. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in statistical analysis if the audit was deleted due to an AQDA that resulted in data deletion.

Overall, the responses of the individual analyzers indicate that as a whole, the network is providing accurate data. Ninety-two percent of the instruments audited in 2001 were found to be operating within the ARB's control limits (+/-15%). The most common causes for audit failure are malfunctions within the instrument and leaks in the sampling system. Instruments operating outside of ARB's control limits resulted in 3,156 days of invalidated data and 127 days of corrected data. Table A1 summarizes the 2001 performance audit results for the criteria pollutants. In 2001, the number of methane and total hydrocarbon audits continued to decrease due to a change in monitoring methodologies (i.e. Bendix to TECO 55) and are not summarized in this report. The TECO 55 is a sophisticated system capable of measuring non-methane hydrocarbons on a real-time continuous basis. Further information about the air monitoring systems and the audit procedures are available at

http://www.arb.ca.gov/aagm/gmosqual/sysaudit/criteria/ga_gas.htm.

Table A1. 2001 Results for Criteria Pollutants Performance Audits Conducted by ARB

Pollutant	Number of Analyzers Audited	Number of AQDAs	Average % Difference	Probabilii 95%UL	ty Limits 95%LL
CO	72	5	-0.2	7.0	-7.4
NO2	91	6	-0.3	10.3	-10.9
O3	149	16	-2.9	4.0	-9.8
SO2	34	3	-0.4	10.6	-11.4
H2S	8	1	-0.6	7.6	-8.8

Source: Quality Assurance Section, Accuracy Estimates

MLD also participates in the U.S. EPA's National Performance Audit Program (NPAP). The results of the NPAP audits, available upon request, are calculated and compiled by the U.S. EPA. The audits differ from our TTP audits in that the gas is introduced at the back of the instrument instead of the probe. Leaks in the probe or manifold are not detected by NPAP audits.

<u>Precision (field)</u>: Precision checks (zero and span) are performed by site operators on a nightly basis to confirm the linear response of the instrument. The zero precision check confirms the instrument's ability to maintain a stable reading. The span precision check confirms the instrument's ability to respond to a known concentration of gas. The degree of variability in each of these nightly measurements is computed as the precision of that instrument's measurements.

Annually, the QAS conducts a precision data analysis as an overall indicator of data quality. The analysis addresses three parameters: precision data submission, precision data validity, and a combination of the two referred to as data usability rates. The precision performance goal for all three parameters is 85%. The submission rate is the number of precision points submitted for a pollutant divided by the expected number of bi-weekly submissions. Data validity is the percent difference of the actual and indicated values of each precision check. These differences should not exceed +/-15% for gaseous analyzers. Usable data rates are determined by multiplying the data submission and data validity rates; and indicate the completeness of verifiable air quality data on the official database. Overall, the precision data submitted met the data validity rate; however, because of the low submission rates, not all pollutants met the 85% performance goal for usable data. Table A2 shows the statewide submission, validity, and usable data rates for each pollutant. For a more detailed description of the usability data rates for each district, please refer to Appendix B.

Table A2. 2001 Criteria Pollutants Precision Analysis Results for California

Pollutant	Submission Rate	Validity Rate	Usable Rate
CO	86%	97%	84%
NO2	91%	99%	90%
O3	84%	95%	82%
SO2	88%	100%	88%
H2S	59%	100%	59%

Source: Quality Assurance Section, Precision Data Analysis

B. Particulate Matter





Particulate Samplers

Particulate matter is a mixture of substances that include elements such as carbon and metals; compounds such as nitrates, organic compounds, and sulfates; and complex mixtures such as diesel exhaust and soil. Particles with an aerodynamic diameter of 10 microns or smaller pose an increased health risk because they can deposit deep in the lung and contain substances that are particularly harmful to human health. Respirable particulate matter (PM10) and fine particulate matter (PM2.5) increase the chance of respiratory disease, lung damage, cancer, and premature death. Particulate matter monitoring is conducted using both manual and continuous type samplers. Manual samplers are operated on a six-day sampling schedule for PM10, and a similar, or more frequent schedule, for PM2.5. ARB's particulate program also includes total suspended particulates (TSP) sulfate, mass (Mexico only), and lead monitoring. Particulate matter is a controlled data set and as such is subject to formal data quality objectives and federal and State regulations. For additional information about the Particulate Matter Monitoring program, visit the Particulate Matter home page at http://www.arb.ca.gov/aagm/partic.htm.

Accuracy (field): The accuracy of particulate samplers is determined using a certified variable orifice (PM10 and TSP), or a calibrated mass flow meter (dichotomous, TEOM, BAM, and PM2.5 samplers) that is certified against a National Institute of Standards and Technology (NIST) traceable flow device or calibrator. Since

an accurate measurement of particulate matter is dependent upon flow rate, the ARB conducts annual flow rate audits at each site. The average percent difference between the sampler flow rates and the audit flow rates represents the combined differences from the certified value of all the individual audit points for each sampler. The upper and lower probability limits represent the expected flow rate accuracy for 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in the statistical analysis shown here if the audit was deleted due to an AQDA that resulted in data invalidation.

Overall, the 2001 flow audit results indicate that the flow rates of samplers in the network are generally within bounds. Ninety-six percent of the instruments audited in 2001 operated within the ARB's control limits. Instruments operating outside the control limits typically had an improper set-point of the mass flow controller or drift that was not discovered. Under normal operation, the set-point of the mass flow controller should compensate for a change in temperature and pressure. Instruments operating outside of ARB's control limits resulted in 757 days of invalidated data and 21 days of corrected data. The 2001 performance audit results are listed below in Table B1. In 2001, only two TSP (Pb) and two dichotomous samplers were audited and thus were not included in the statistical summaries. The TSP data accuracy estimates include samplers that analyze for mass and/or sulfates. The BAM data accuracy estimates reflect samplers operated as BAM PM10.

Table B1. 2001 Results for Particulate Sampler Performance Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Number of AQDAs	Average % Difference	Probabili 95%UL	ty Limits 95%LL
PM2.5	100	3	-0.4	3.7	-4.5
PM10	147	2	-0.7	5.7	-7.1
PM10 Partisol	21	0	-0.1	4.1	-4.3
TEOM	36	6	-0.7	6.3	-7.7
BAM PM10	6	3	-2.2	3.3	-7.7
TSP	12	0	-0.6	7.8	-9.0

Source: Quality Assurance Section, Accuracy Estimates

<u>Precision (field)</u>: Precision data for non-continuous particulate samplers is obtained through collocated sampling whereby two identical samplers are operated side-by-side and the same laboratory conducts filter analyses. Collocated samplers are located at selected sites and are intended to represent overall network precision. Validity of the data is based on the percent difference of the mass concentrations of the two samplers. In 2001, collocated PM10 samplers were operated at Bakersfield-California, Visalia, Corcoran-Patterson, and Taft-College sites. Collocated dichotomous samplers were operated at the Fresno-First site. Collocated TSP samplers were operated at the Bakersfield-California and San Diego 12th St. site. Collocated PM2.5 samplers were operated at Fresno-First, South Lake Tahoe, Truckee, and Yuba City sites.

Particulate samplers (collocated PM10, dichotomous, and TSP) must have mass concentrations greater than or equal to $20\mu g/m3$ to be used in data validity calculations. The difference between the mass concentrations must be no greater than $5\mu g/m3$. If the mass concentrations are greater than $80\mu g/m3$, the difference must be within +/-7% of each other. TSP (Pb) samplers must have both mass concentrations greater than or equal to $0.15\mu g/m3$ to be used in data validity calculations. For collocated PM2.5 samplers, data validity is based on the sampler's coefficient of variation, which cannot exceed 10%. Both sample masses must also be greater than $6\mu g/m3$.

Continuous TEOM and BAM precision is based on the comparison of the sampler's/analyzer's indicated and actual flow rates. The differences between the flow

rates must be within +/-15%. The particulate sampler precision analysis results for 2001 are available in Table B2.

Overall, the precision data submitted met the data validity rate for most pollutants; however, because of low submission rates, the 85% performance goal for usable data rates was not met. For a more detailed description of the usability data rates for each district, please refer to Appendix B.

Table B2. 2001 Particulate Sampler Precision Analysis Results for California

Pollutant	Submission Rate	Validity Rate	Usable Rate
PM2.5	59%	95%	56%
PM10	69%	89%	62%
PM10 Partisol	100%	82%	82%
Dichotomous	96%	50%	48%
TEOM	39%	91%	35%
BAM PM10	NA	NA	NA
TSP	NA	NA	NA

Source: Quality Assurance Section, Precision Data Analysis

Accuracy (lab): Annual performance audits for PM10 and PM2.5 mass analysis programs include an on-site check and assessment of the filter weighing balance, relative humidity and temperature sensors, and their documentation. The performance audits conducted in 2001 found that the district programs were operating in accordance with U.S. EPA guidelines and that the data were of good quality and should be considered data-for-record. Table B3 summarizes the performance audit findings.

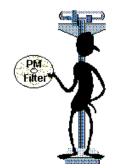


Table B3. 2001 PM10 and PM2.5 Particulate Matter Mass Analysis Performance Audits

District	Conducted	Pass/Fail
California Air Resources Board (PM10 and PM2.5)	2/8/01	Pass
Bay Area AQMD (PM 2.5 only)	12/12/01	Pass
Great Basin	8/24/01	Pass
Monterey Bay Unified APCD	9/20/01	Pass
North Coast Unified AQMD	7/31/01	Pass
No. Sierra AQMD	8/27/01	Pass
No. Sonoma Co. APCD	6/26/01	Pass
Placer Co. APCD	2/9/01	Pass
Sacramento Metropolitan AQMD	10/16/01	Pass
San Luis Obispo APCD	4/19/01	Pass
San Diego County APCD (PM 2.5 only)	9/10/01	Pass
Santa Barbara Co. APCD	6/13/01	Pass
Siskiyou Co. APCD	7/13/01	Pass
South Coast AQMD (PM 2.5 only)	10/30/01	Pass
Ventura Co. APCD	6/4/01	Pass

Laboratories supporting the PM2.5 mass analysis program first completed a precertification process that included a questionnaire, an on-site visit, and a performance audit of the laboratory's microbalance and relative humidity (RH) and temperature sensors. Pre-certification standards must be met before the laboratory was able to submit PM2.5 data to the U.S. EPA's Air Quality System (AQS). All laboratories met the pre-certification conditions. Full system audits are initiated on qualifying laboratories. One full PM2.5 system audit was conducted in 2001. The system audit findings concluded that the Lake County AQMD PM2.5 program satisfied the U.S. EPA regulations and that the data were of good quality and should be considered data-for-record.

Laboratory audits were are also conducted for the PM10 ions program using NIST-traceable filter standards for nitrate (NO3-), sulfate (SO4⁻²), chloride (CI-), ammonium (NH4+), and potassium (K+). Audit results for the Northern Laboratory Branch's (NLB) ions program (conducted in the 1st and 3rd quarters of 2001) were within the targeted +/- 20% control limit established for the audit procedure. Laboratory audits for the TSP (Pb) program were conducted using NIST-traceable standards. The 2001 audit results were found to be within ARB's +/- 20% control limits indicating that NLB is accurately identifying TSP (Pb).

MLD also participates in the field and laboratory NPAP programs for PM10, however, the U.S. EPA compiles the NPAP audit results. The results are available upon request from the U.S. EPA. The federal audit program covers only a portion of the PM10 network sites in California. The ARB audit results; however, are compared to the NPAP results to understand and improve the audit program.

<u>Precision (lab)</u>: Laboratories perform various quality control tasks to ensure that quality data are produced. Tasks include duplicate weighings on exposed and unexposed filters, replicate analysis on every 10th filter, and a calibration of the balance before each weighing session. Upon receipt of particulate matter filters from the field, laboratory staff have up to 30 days to analyze the PM10 and PM2.5 samples. Filters are visually inspected for pinholes, loose material, poor workmanship, discoloration, non-uniformity, and irregularities, and are equilibrated in a controlled environment for a minimum of 24 hours prior to the filters are weighed. If room conditions are not within the established U.S. EPA control limits, weighings are done only after the proper environment is re-established and maintained for 24 hours.

In 2001, there were no occurrences in which ARB's laboratory balance room was outside of control limits. The analytical precision results indicate that ARB is providing precise particulate matter data. Tables B4 and B5 show the unexposed and exposed filter replicate results for ARB's laboratory in 2001.

Table B4. 2001 Summary of ARB's Unexposed Filter Mass Replicates

QC Check	PM10	Dichotomous	PM2.5
# of pre-weighed filters	3999	180	3272
# of replicates analyses	500	18	352
% replicates weighing conducted	12.5	10.0	10.8
# of replicates out of range	0	0	0

Source: Inorganics Laboratory Section, Quality Control Report

Table B5. 2001 Summary of ARB's Exposed Filter Mass Replicates

QC Check	PM10	Dichotomous	PM2.5
# of post weighed filters	3562	208	2253
# of replicates analyses	396	34	245
% replicates weighing conducted	11.1	16.4	10.9
# of replicates out of range	0	0	0

Source: Inorganics Laboratory Section, Quality Control Report

C. Toxic Air Contaminants

In 1985, the ARB established an ambient volatile organic compound (VOC) toxic monitoring network in major urban areas of the state to determine the average annual concentrations of toxic air contaminants (TAC). The program was established to assess the effectiveness of control measures in reducing air toxics exposures. Compounds identified as TACs vaporize at ambient temperatures, play a critical role in the formation of ozone, and have adverse chronic and acute health effects. Sources of TACs include motor vehicle exhaust, waste burning, gasoline marketing, industrial and consumer products, pesticides, industrial processes, degreasing operations, pharmaceutical manufacturing, and dry cleaning operations.



Stainless Steel Toxics Canister

Under the current ARB sampling schedule, ambient air is collected in a stainless steel canister (or cartridge) every 12 days over a 24 hour sampling period at each of the network stations. Toxic particulate samples are also collected and analyzed for toxic air contaminants to support the California Toxic Air Contaminant Identification and Control program. By using a low-flow multi-channel sampler capable of sampling onto filters or cartridges, ambient air is collected and analyzed for carbonyl and polycyclic aromatic hydrocarbons (PAH) compounds and toxic metals. The quality of the air toxic data set is governed by a series of quality assurance activities, including audits. However, because this is a descriptive data set, no mandatory corrections are made to the data based on audit results. The laboratory and monitoring staff are made aware of any

exceedance found during an audit, and every effort is made to ensure that the data collected is as accurate as possible.

The audit programs contained three elements in 2001: TTP performance audits, laboratory audits, and a whole air comparison check. The audit results and several papers that discuss these elements of the QA program in detail are available at http://www.arb.ca.gov/aagm/toxics.htm.

<u>Accuracy (field)</u>: TTP performance audits for VOCs are typically conducted annually at each air toxic site to assess the accuracy of the total measurement system. System errors can include contamination during transport, artifacts created by the sample pump or the probe, and laboratory bias.

The 2001 TTP performance audits results are shown in Table C1. The values represent the average percent difference for each compound from all audits conducted at ARB sites. The 2001 audit results indicated exceedances of the audit criteria (+/-20%) for ethylbenzene (-39.8%), m/p-xylene (22.9%), and 1,3-butadiene (-22.1%). QAS recommended that the laboratory investigate the cause of the exceedances. As a result of trouble shooting efforts, ARB's Organics Laboratory (OLS) staff discovered that the NIST certified concentrations of ethylbenzene and m/p-xylene, in their calibration gas, were incorrect, as determined by using a different NIST certified calibration cylinder and comparing results. Staff also noticed that the stability of 1,3-butadiene in the calibration cylinder had degraded over time. After switching NIST calibration cylinders, audit results for all compounds were within QAS audit criteria in 2002.

Table C1. 2001 Toxic Air Contaminants TTP Audit Results for California's Toxic's Network

	Т	TP
	Avg %	Std
Compound	Diff	Dev
Benzene	-5.9	4.3
1,3-Butadiene	-22.1	5.0
Carbon Tetrachloride	-9.1	3.8
Chloroform	-7.3	5.7
ortho-Dichlorobenzene	-18.7	16.5
Ethylbenzene	-39.8	3.7
Methyl Chloroform	-5.3	4.0
Methylene Chloride	1.6	8.6
Perchloroethylene	-14.0	7.3
Styrene	-18.7	8.8
Toluene	-7.4	5.8
Trichloroethylene	-11.9	4.8
m/p-Xylene	22.9	8.9
o-Xylene	-7.5	4.8

In 2001, a whole air comparison check was also conducted to compare the analytical methods used by all the laboratories that measure ambient concentrations of toxic

compounds. The purpose of the comparison check is to confirm the comparability of the analytical methods currently used by those laboratories measuring ambient concentrations of gaseous toxic compounds. A specially designed sampler draws ambient air for 3 hours, filling up to 10 canisters at a time, to an approximate pressure of 14 pounds per square inch gauge (psig) each. A canister is sent to each laboratory for analysis. The laboratories follow their standard operating procedures in assaying the contents and report their results to the QAS for comparison against other participating laboratories. As can be seen below in Figure C1 – C3, the ten participating laboratory's responses compared well for most compounds. If a laboratory's response for a compound was significantly different from the other laboratories, the laboratory was asked to investigate and report the cause.

Figure C1. 2001 Whole Air Comparison Check for Toxic Air Contaminants (Continued on next page)

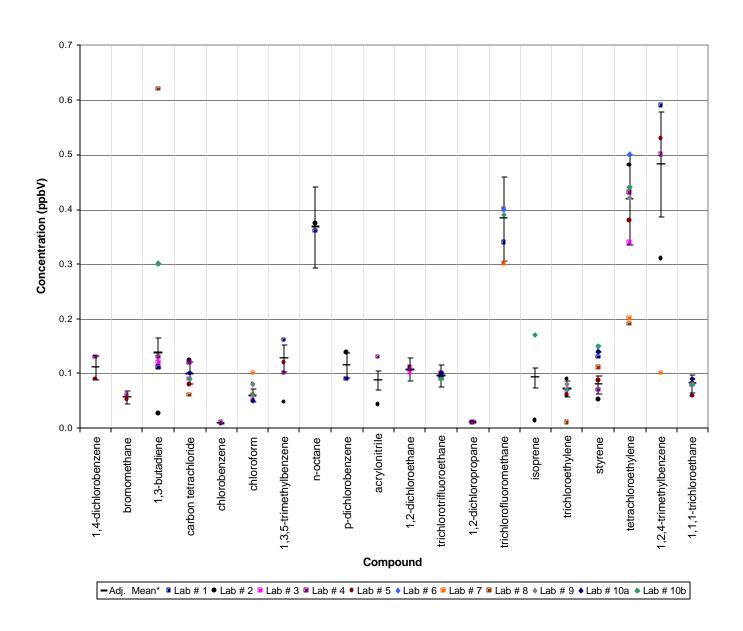


Figure C2. 2001 Whole Air Comparison Check for Toxic Air Contaminants (Continued on next page)

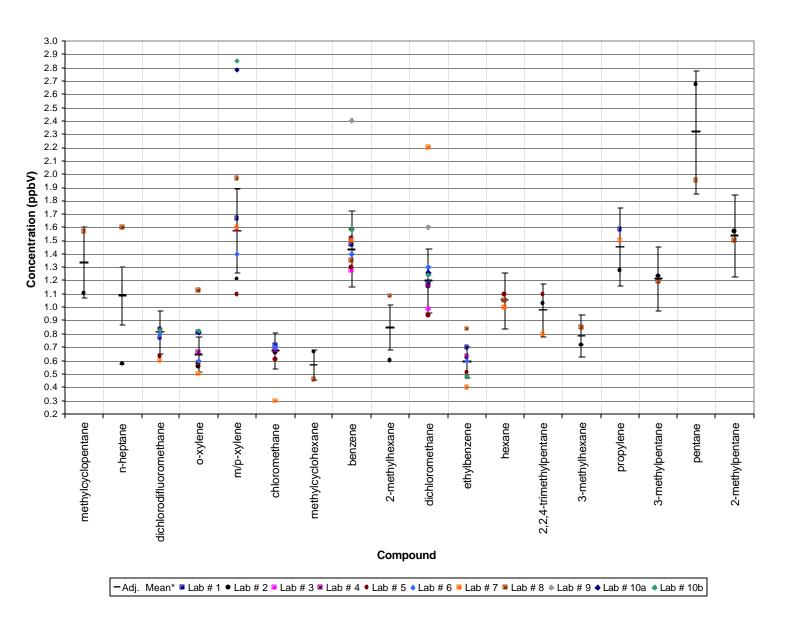
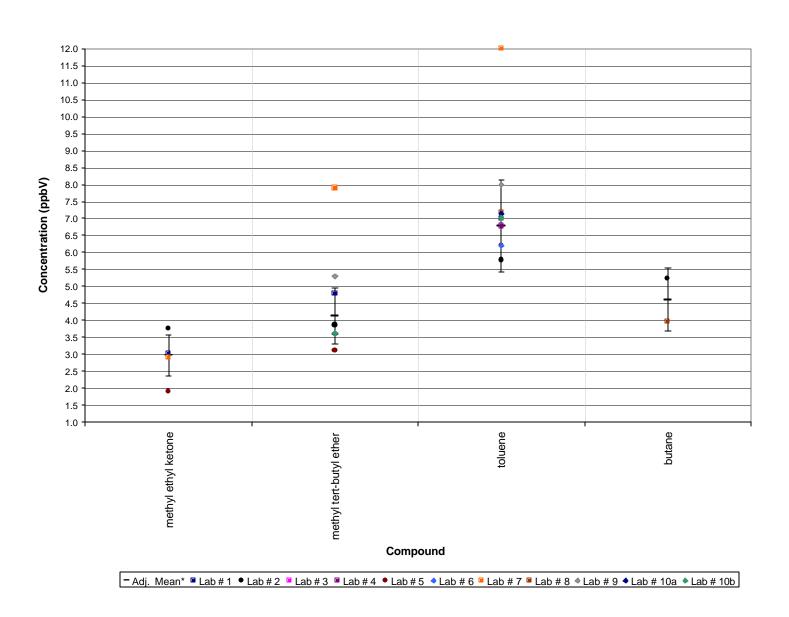


Figure C3. 2001 Whole Air Comparison Check for Toxic Air Contaminants



Flow audits of the toxic metal and carbonyl sampler (shown right) are typically conducted annually at each site to ensure the accuracy of measuring toxic metals and carbonyl compounds. Flow rates are a determining factor in calculating concentration and are included as part of the quality assurance program.

Overall, the 2001 results indicate that the samplers maintained stable flows. Ninety-four percent of the instruments audited operated within the ARB's control limits of +/-15%. Although toxics data are a descriptive data set, AQDAs are issued based on the operating parameters of the sampler. Corrections are made to the data if an audit is found to be outside the ARB's control limits. Instruments operating outside of ARB's control limits resulted in 60 days of invalidated flow rate data.



Toxic Metals and Carbonyl Sampler

Table C2 shows the differences from the certified value of the individual audit points for each pollutant. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single analyzer's individual percent differences for all audit test levels at a single site. Audit results were not used in the statistical analysis shown below if the ambient data was deleted due to an AQDA.

Table C2. 2001 Results for Toxic Air Sampler Flow Rate Performance Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Number of AQDAs	Average % Difference	Probabi 95%UL	lity Limits 95%LL
Cr6+	29	1	0.5	7.7	-6.7
Total Metals	31	2	0.2	7.8	-7.4
Aldehydes	31	3	0.4	9.2	-8.4

Source: Quality Assurance Section, Accuracy Estimates

Accuracy (lab): Laboratory performance audits are conducted annually to determine the accuracy of a laboratory to measure ambient VOC concentrations. Summary statistics of ARB's audit results are shown in Table C3. The percent difference presented in the table represents the average difference between the laboratory's measured value and the NIST certified value. The 2001 audit results indicated exceedances of the audit criteria (+/-20%) for ethylbenzene (-34.7%), m/p-xylene (37.5%). QAS recommended that the laboratory investigate the cause of the exceedances. As a result of trouble shooting efforts, OLS staff discovered that the NIST certified concentrations of ethylbenzene and m/p-xylene, in their calibration gas, were incorrect, as determined by using a different NIST certified calibration cylinder and comparing results. After switching NIST calibration cylinders, audit results for all compounds were within QAS audit criteria in 2002.

In addition to meet the demands of both the TAC and the Children's Environmental Health Protection Program (SB 25) networks, the laboratory upgraded to a more advanced gas chromatography/mass spectrometry (GC/MS) technique capable of handling an increased workload. The new analytical technique enabled the laboratory to analyze a more expanded list of target compounds with lower limits of detection (LODs).

Table C3. ARB's 2001 Toxic Air Contaminants Laboratory Performance Audit Results

	ARB Laboratory
Compound	% Diff
Benzene	-1.9
Carbon Tetrachloride	10.8
1,3-Butadiene	0.0
Chloroform	-11.3
ortho-Dichlorobenzene	3.9
Ethylbenzene	-34.7
Methyl Chloroform	-3.4
Methylene Chloride	-3.9
Perchloroethylene	-7.5
Toluene	-1.4
Styrene	-12.5
Methyl tert-Butyl Ether	-2.2
Trichloroethylene	-9.2
m/p-Xylene	37.5
o-Xylene	7.5

<u>Precision (field and lab)</u>: As part of the TAC Program laboratory analyses, internal QC techniques such as blanks, control samples, and duplicate samples are applied to ensure the precision of the analytical methods and that the toxics data are within statistical control. Precision data for non-continuous toxic particulate samplers are obtained through collocated sampling whereby two identical samplers operate side-by-side simultaneously and the same laboratory conducts filter analyses. Collocated toxic samplers are located at selected sites and are intended to represent overall network precision. Collocated samplers, located at Bakersfield-California and Riverside-Rubidoux monitoring stations are intended to represent overall network precision.

In 2001, all compounds analyzed were well within their respective control limits and results for blanks, spikes, and duplicate samples established in the Laboratory QC Manual. Duplicate analyses were performed on 10% of the toxic samples. In 2001, all duplicate results (concentrations must be greater than five times the published LODs) were within the established limits for all target analytes. Data exceeding duplicate criteria of three times the assigned percent relative standard deviation (from control samples collected during the control limit evaluation) are deleted from the toxics database and samples reanalyzed.

Stainless steel canisters used to collect ambient air samples are also checked for contamination. Canisters are analyzed for aromatic and halogenated hydrocarbons. One canister per batch of eight is assayed to ensure individual compound measurements fall below the limit of detection. In the event a compound exceeds canister cleanliness criteria, the canister and all other canisters represented in the batch are re-cleaned until compounds meet the cleanliness criteria. In addition, Xontech 910A air samplers are checked for cleanliness. Failed air collection media are re-cleaned and re-tested until they pass Xontech 910A cleanliness criteria (Xontech 910A checks are independent of canister batch checks). Overall, the network is providing precise toxic air contaminants data.

The toxics audit results and several papers that discuss these elements of the QA program in detail are available at http://www.arb.ca.gov/aaqm/toxics.htm.

D. Non-Methane Hydrocarbons

PHOTOCHEMICAL ASSESSMENT MONITORING STATIONS

In 1989, ARB began a routine seasonal sampling program to gather information about non-methane hydrocarbon (NMHC) species that were precursors to ozone formation in high ozone areas. In 1994, Federal regulations required states to establish photochemical assessment monitoring stations (PAMS) as part of their State Implementation Plan monitoring networks in areas designated as serious or higher for ozone. Monitoring is to continue until the ozone standard is reached. The PAMS program is intended to supplement ozone monitoring and add detailed sampling for its precursors. PAMS sites collect data on ozone,



oxides of nitrogen, real-time total NMHC, speciated hydrocarbons, carbonyls, and various ground level and aloft meteorological parameters. As this is a descriptive data set, there are currently no mandatory data quality objectives or regulations for the data. However, efforts are made to ensure that accurate data are collected and that the analyzers are operating within ARB's audit standards. In 2001, the ARB's OLS supported the Fresno-First Street and the Los Angeles-North Main Street air monitoring stations.

In July 2001, the QAS also conducted a system audit of the ARB's PAMS program. The PAMS system audit is an on-site review and inspection of field sites and laboratory operations to assess its compliance with established regulations governing the collection, analysis, validation, and reporting of PAMS sampling data. The system audit is facilitated by the use of a questionnaire designed to provide information about specific portions of the overall program. The QAS review included, but was not limited to, the following: network management, field operations, laboratory operations, data and record keeping, and quality assurance/quality control. The audit found that the ARB's PAMS program is operating within the U.S. EPA guidelines and that the data submitted to the AQS should be considered good quality data and data-for-record.

Three types of ongoing hydrocarbon performance audits are conducted (laboratory, TTP sampler, and TTP continuous analyzer) that support the canister-type collection system and the real-time analyzers. However, due to limited resources in the 2001

PAMS season, fewer TTP audits were conducted. A cross-check is also run by the QAS that allows all laboratories to compare their results from a *whole air sample* representing an identical parcel of air. The whole air sample element of the QA was added after the 1997 South Coast Ozone Study and uses a system developed by QAS staff. Staff presented a paper on the program at the 2000 International Symposium on the Measurement of Toxic and Related Air Pollutants. A copy of the paper as well as other information about the PAMS quality assurance program is available at http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/qa_nmhc.htm.

Accuracy (lab and field):

Laboratory performance audits are conducted annually to assess the participating laboratory's ability to measure ambient levels of hydrocarbons. TTP Sampler performance audits are conducted annually at each monitoring site to assess the integrity of the sampling, analysis, and transport system. In addition, blank samples are periodically collected to check for contamination. Evaluation of the blank samples collected in 2001 indicated potential contamination of 2-methylpropane and 3-methylhexane audit results. At the time of the audits, the zero air system used by the QAS showed high levels of 2-methylpropane and 3-methylhexane. The QAS received help from the manufacturer and Operations Support Section staff and took corrective action to clean and certify the system to ensure future contamination would not occur. The effected audit responses were not included in the statistical analyses or audit reports.

The 2001 laboratory and TTP sampler performance audit results are shown in Table D1. The average percent difference represents the combined differences from the certified value for all the sites and laboratories audited. Laboratories exceeding the ARB's control limits of +/-20% were asked to investigate and report the cause of the exceedance(s). The 2001 laboratory performance audit results show that low ethane recoveries were a chronic problem for one of the laboratories, which resulted in an overall high standard deviation. The TTP sampler audit results show a high degree of fluctuation among standard deviations and some compounds exceeded ARB's control limits of +/-20%. Laboratories exceeding the ARB's control limits of +/-20% were asked to investigate and report the cause of the exceedance(s). Corrective action measures taken by the laboratories (and air monitoring staff) included: re-integration of analytical peaks, verification of acceptable quality control results, investigation into potential canister contamination, change-out of sampling lines, addition of assist pumps, and investigation into dilution unit. One of the laboratories experienced insufficient humidification, which contributed to low recoveries for many of the heavy compounds.

Table D1. 2001 TTP Sampler and Laboratory NMHC Audit Results for California's PAMS Network

	Т	ГР		Labo	ratory
	Avg	Std		Avg	Std
Compound	%Diff	Dev	Compound	%Diff	Dev
Ethane	-9.7	19.4	Ethane	-4.7	21.8
Ethene	-3.4	9.4	Propane	0.2	4.1
Propane	-0.4	12.2	Propene	-1.2	5.0
Butene	-12.5	20.0	2-Methylpropane	0.2	4.5
Pentane	-8.9	13.7	Butane	0.5	3.3
2-Methylpentane	-1.2	6.9	2-Methylpropene	2.5	3.0
Hexane	23.6	62.2	2-Methylbutane	2.2	2.5
Benzene	-1.6	9.3	Pentane	1.1	4.8
3-Methylhexane	0.4	6.2	1-Pentene	-2.3	4.1
2,2,4-Trimethylpentane	-1.4	6.4	Hexane	1.9	2.8
Methylcyclohexane	15.8	37.6	Benzene	3.1	2.7
Toluene	12.6	56.9	Octane	3.4	2.2
Octane	1.2	8.0	Toluene	0.9	5.4
Ethylbenzene	-10.4	14.5	o-Xylene	0.2	4.4
m/p-Xylene	-11.8	16.6	Decane	-1.6	3.5
o-Xylene	-13.3	18.1			
Decane	-12.8	28.0			
3-Methylheptane	-2.8	5.4			
n-Propylbenzene	-14.0	24.8			
1,2,3-Trimethylbenzene	-21.9	26.9			

TTP continuous NMHC analyzer performance audits include audits of total NMHC analyzers (i.e., TECO 55). The 2001 TTP continuous analyzer NMHC PAMS audit results are shown in Table D2. The purpose of this table is to estimate the accuracy of the hydrocarbon data in the database. The upper and lower probability limits represent the expected accuracy of 95 percent of all the analyzer's individual percent differences for all audit test levels at a single site. Based on the audit results, sixty-nine percent of the instruments audited were found to be operating within the ARB's control limits +/-15%. Audit results were not used in the statistical analysis if the audit was deleted due to an AQDA that resulted in data invalidation. Out of control events were typically due to instruments that were inoperable at time of the audit, contamination of the analyzers clean air source, and inconsistent span check readings. Instruments operating outside of ARB's control limits resulted in 1,802 days of invalidated data.

Table D2. 2001 Results for TTP Continuous Analyzer NMHC PAMS Audits

Pollutant	Number of Analyzers Audited	Number of AQDAs	Average % Difference	Probabili 95%UL	ty Limits 95%LL
NMHC	11	5	0.1	12.1	-11.9.

Source: Quality Assurance Section, Accuracy Estimates

The Whole Air Sampler performance checks are a valuable complement to the TTP and laboratory audits. Specifically, they are a means of assessing performance using a sample that includes non-target species and other aspects of a real world sample that could potentially affect sample results. It involves all California PAMS laboratories that measure ambient concentrations of hydrocarbons as well as others choosing to participate. The performance check uses a specially designed sampler that draws ambient air for 3 hours into 10 canisters at a time. They reach approximately 14 pounds per square inch gauge (psig) each. This replicates a normal sample duration and pressure. A canister is sent to each participating laboratory for speciated NMHC analysis. The laboratories follow their standard operating procedures in assaying the contents and report their results to the QAS.

The 2001 Whole Air Comparison Check results are shown in Figure D1. Based on the results, the laboratory responses compared well for most compounds. If a laboratory's response for a compound was significantly different from the other laboratories, the laboratory was asked to investigate the cause. The results for ethane, which were of concern in the TTP audits, were relatively good with very little variation in the whole air sample. The QAS plans to track this anomaly to determine the difference between the two audits. The whole air comparison check results are available at http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/nmhc/whole/wholetable.htm.

Figure D1. 2001 Whole Air Comparison Check (Continued on next page)

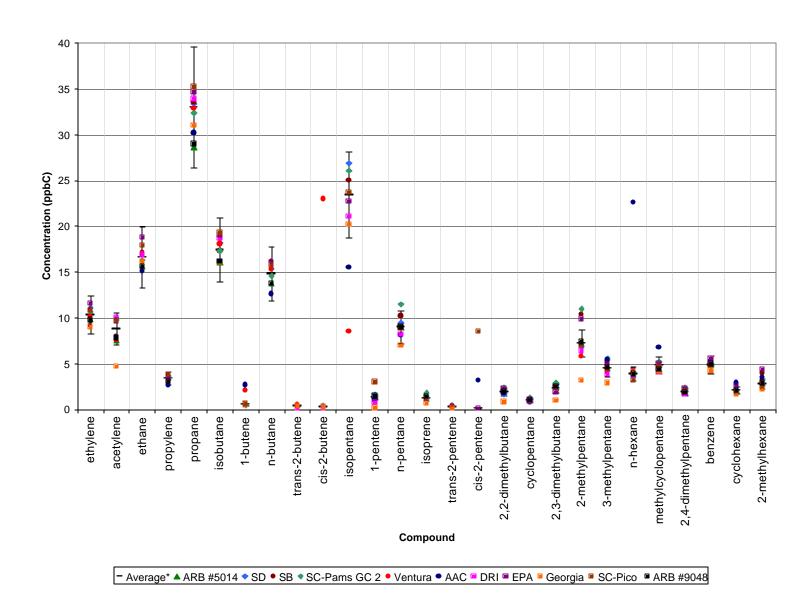
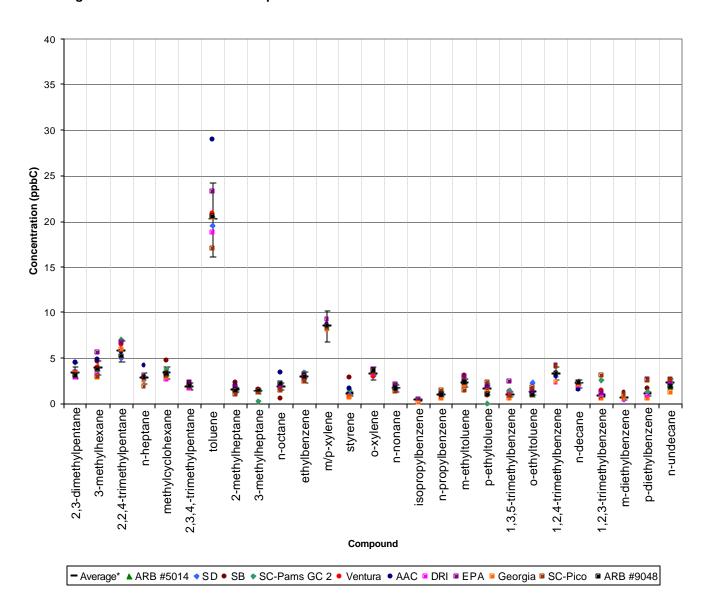


Figure D1. 2001 Whole Air Comparison Check



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The QAS also conducts carbonyl sampler flow and TTP audits. Because the accuracy of measuring carbonyl compounds is dependent upon the sampling flow rate, flow audits of the three channels are conducted in conjunction with the TTP audits. All samplers audited were found to have flow rates operating within the ARB's control limits of +/-10%. In previous years, problems with samplers operating outside the control limits were primarily due to improper calibration of the mass flow controllers. TTP carbonyl performance audits are typically conducted annually by QAS to assess the accuracy of the total measurement system, including errors inherent in transport, effects of sample pump and probe, and laboratory error. The upper and lower probability limits represent the expected accuracy of 95% of all the single analyzer's individual percent differences for all audit test levels at a single site. The 2001 audit results, shown in Tables D3 and D4 indicate that the PAMS carbonyl samplers maintain consistent and accurate flow rates and that the network is performing well and is accurately measuring carbonyl compounds present in ambient air.

Table D3. 2001 Results for Carbonyl Sampler Flow Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Average % Difference	Probability 95%UL	y Limits 95%LL
Carbonyl Channel A	3	1.2	6.5	-4.1
Carbonyl Channel B	3	3.3	6.3	0.3
Carbonyl Channel C	3	4.8	15.5	-5.9

Source: Quality Assurance Section, Accuracy Estimates

Table D4. 2001 Results for Carbonyl TTP Sampler Performance Audits Conducted by ARB

Pollutant	Number of Samplers Audited	Average % Difference	Probabil 95%UL	ity Limits 95%LL
Carbonyl	8	-5.2	5.5	-16.0

Source: Quality Assurance Section, Accuracy Estimates

<u>Precision (lab and field)</u>: Precision for the manual PAMS canister and aldehyde samplers is obtained through collocated sampling and occurs at selected PAMS sites. Collocated sampling consists of two identical samplers running side by side analyzed by the same laboratory. The data generated represent precision for the network as a whole. Each of the PAMS laboratories selects one site where a duplicate canister of ambient air is collected (using two separate sampling systems). In 2001, a collocated sampler was located at the Fresno-First site to represent the precision of the ARB network.

In addition, the laboratories performed daily duplicate analyses on at least 10% of the total number of ambient samples.

The precision of PAMS carbonyls data is also confirmed through collocated sampling in much the same manner as the canisters. The laboratory analyzes two collocated cartridges from one sampling system that has two sampling channels.

The laboratory also analyzes blank and spiked samples for formaldehyde, acetaldehyde, and acetone and performs duplicate analyses on 10% of the ambient cartridge samples. The blank data is obtained by attaching a cartridge to an unused channel of the sampler. A blank sample is collected for each scheduled trend day and positive analytical responses are used to correct ambient air carbonyl concentrations (the average trip blank values for the respective compounds are subtracted from measured ambient concentrations) for any contamination that may have occurred during shipping and handling. Spiked samples are generally made at a frequency of one spike per analytical run and are done after the cartridges are desorbed.

Because only 86 ambient air samples were collected during the 2001 PAMS hydrocarbon season for the ARB laboratory (collected at Fresno-First and Los Angeles North Main St. sites), summary data for collocated, duplicates, blanks, and spiked samples analyses were not generated. The raw data are available in the Laboratory Information Management System or upon request.

Information about the carbonyl program is available at http://www.arb.ca.gov/aaqm/qmosqual/perfaudit/carbonyl.htm.

MOTOR VEHICLE EXHAUST PROGRAM

The QAS motor vehicle exhaust audit program supports ARB's efforts in determining the reactivity of fuel components found in automotive exhaust samples. The exhaust and fuels information can be compared to the regulatory standard for non-methane organic gases tail-pipe emissions, fuel composition, and a number of ozone precursors. Special studies are currently being conducted to determine emissions generated from vehicles operated under manufacturers recommendations.



Emissions Sampling

<u>Accuracy</u>: Laboratory performance audits are conducted annually of the Southern Laboratory Branch of ARB for components of motor vehicle exhaust collected while a vehicle was operated on a dynomometer. In 2001, five of the laboratory's six gas chromatographs (GC) were audited as well as the total NMHC analysis system (pre-concentration direct flame ionization detector (PDFID)). Audit results for the PDFID system were -3.2% from true (sum of all species).

Figure D1 illustrates the results for speciated hydrocarbon audits for 2001. The average percent differences of the audit values and laboratory results were calculated using the average reported concentration for each GC. The audit results indicated that the speciated compounds for each GC were within +/-20% of the NIST traceable cylinder. Overall, the laboratory performed well and provides accurate data to support the motor

vehicle exhaust program. Audit results have remained consistent over the last two years.

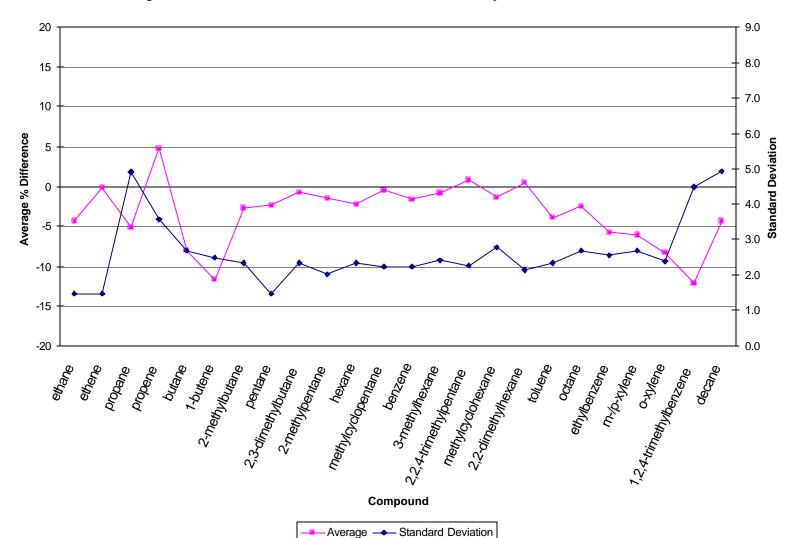


Figure D1. ARB's 2001 Motor Vehicle Exhaust Laboratory NMHC Audit Results

E. Pesticides



Pesticides Sampler

Ambient and near field (application) pesticide monitoring is performed by the ARB at the request of the California Department of Pesticide Regulation (DPR) to determine the airborne concentration of pesticides at times and in areas of pesticide use. Some of the active ingredients found in pesticides are known to cause a wide range of adverse health effects in people, vegetation, and wildlife. The data are descriptive sets and are not subject to strict data quality objectives.

Two types of monitoring are conducted; ambient and application. During ambient, or community air measurements, ARB collects samples at approximately half a dozen locations (usually schools or other public buildings) in communities near agricultural areas expected to receive applications of the pesticide. Samples of 24 hours in duration

are typically collected for four days per week for four or more consecutive weeks. Application-site monitoring (e.g., sampling before and after a specific application), samples are collected immediately before, during, and for approximately 72 hours following pesticide application.

In 2001, the DPR requested that the ARB conduct ambient air monitoring for the soil fumigants methyl bromide, 1,3-dichloropropene (Telone), chloropicrin, and the metamsodium breakdown products MITC and MIC. Ambient monitoring was conducted in Kern (June 30, 2001 to August 31, 2001) and Monterey and Santa Cruz (September 8, 2001 to December 8, 2001) counties. Sampling at a 'background' site in Santa Cruz was also conducted for one week in late September. The purpose of the background sampling was to determine the ambient concentrations of methyl bromide in an area not impacted by the regional agricultural use of the fumigant. The times of monitoring correspond with the use of two soil fumigants prior to planting a variety of crops. Air samples for methyl bromide and 1, 3-dichloropropene were collected using evacuated 6-liter Silcosteel® canisters. Chloropicrin, MITC, and MIC sampling was conducted using charcoal tubes.

Accuracy (field): Since accurate measurement of pesticides in ambient air is dependent upon flow rate, flow audits are performed on pesticide samplers after calibration and prior to sampling to assure data quality. Table E1 represents the 2001 pesticide flow rate audit data. The flow audit results indicate that the program is providing accurate flow rate data.

Table E1. ARB's 2001 Pesticide Flow Rate Audit Results

Number of Samplers Audited	Average % Difference	Std Dev
97	1.5	7.3

<u>Precision (lab)</u>: Field quality control tasks are conducted for ambient and application monitoring to assess system precision for a variety of pesticides used. Collocated samplers are used and duplicate analyses are performed on 10% of the samples. These tasks are for evaluation purposes, as there are no formal data quality objectives or established criteria.

In Kern County, 42 collocated pairs of canister samples were collected for both methyl 1,3-dichloropropene. relative and The percent (RPD=(difference /average) X 100) provides an indication of the precision of the monitoring method (i.e., the lower the RPD the better the precision). The RPDs of the data pairs for methyl bromide (for which collocated sample pairs had both results above the quantitation limit) averaged 7.4% and ranged from 0.8% to 42.3%. The RPDs of the data pairs for 1,3-dichloropropene (for which collocated sample pairs had both results above the quantitation limit) averaged 18.0% and ranged from 2.1% to 70.3%. addition, 48 collocated pairs of charcoal tube samples were collected for chloropicrin, MITC, and MIC. Among all the collocated MITC pairs analyzed, 25 pairs had both MITC results above the quantitation limit. Only one pair of chlorpicrin collocated samples, 12% RPD, had both chloropicrin results above the quantitation limit. RPDs for MIC collocated pairs could not be determined because the majority of sample pairs had results below the method detection limit. The RPDs of MITC data pairs averaged 5.0% and ranged from 0.1% to 23.8%. Precision for the MIC monitoring method could not be determined because the sample measurements were not above the quantitation limit. RPDs for collocated chloropicrin and MITC samples indicate acceptable precision for the methods.

In Monterey and Santa Cruz counties, 42 collocated pairs of canister samples were collected for methyl bromide and 1,3-dichloropropene. The RPDs of the data pairs for methyl bromide (for which collocated sample pairs had both results above the quantitation limit) averaged 7.0% and ranged 0.0% to 29.0%. The RPDs of the data pairs for 1,3-dichloropropene (for which collocated sample pairs had both results above the quantitation limit) averaged 20.0% and ranged from and 0.0% to 90.0%. In addition, 48 collocated pairs of charcoal tube samples were collected for chloropicrin, MITC, and MIC. Among all the collocated chloropicrin pairs analyzed, 37 pairs had both MITC results above the quantitation limit. The average RPD for both MITC and MIC collocated pairs could not be determined because the majority of sample pairs had results below the method detection limit. The RPDs of chloropicrin data pairs averaged 12.0% and ranged from 0.0% to 48.0%. Precision for the MITC and MIC monitoring method could not be determined because the sample measurements were not above the quantitation limit. RPDs for collocated chloropicrin samples indicate acceptable precision for the methods.

Accuracy (lab): The QAS does not conduct performance audits at this time; however, laboratory quality control tasks are conducted to assess the accuracy of the sampling and analytical methods. These tasks include analyses of field spikes, trip spikes (standards), laboratory spikes and trip blanks. These tasks are for evaluation purposes, as there are no formal data quality objectives or established criteria. Two instruments, MSD 3 and MSD 4, were used for laboratory analyses of the canister samples resulting in two sets of results. Tables E2A and E2B represent the laboratory, trip, and field spikes results for methyl bromide, 1,3-dichloropropene, chloropicrin, MITC, and MIC conducted in Kern County (canister and cartridge samples). Tables E3A and E3B represent the laboratory, trip, and field spikes results for methyl bromide, 1,3-dichloropropene, chloropicrin, MITC, and MIC conducted in Monterey and Santa Cruz counties (canister and cartridge samples).

The laboratory, trip, and field spike recoveries for MITC were consistent among sample groups but were generally low. According to the laboratory, low spike recoveries for MITC were caused in part by low extraction efficiency. Due to the low recoveries, the concentrations of MITC in sampled air may be underestimated by the method.

The laboratory, trip, and field spike recoveries for MIC were generally high. According to the laboratory, high recoveries for MIC were due to both a narrow retention time window and the presence of interfering peaks. The true concentrations of MIC in sampled air may be different from the measured values.

The laboratory, trip, and field spikes results for methyl bromide, 1,3-dichloropropene, and chloropicrin indicate that the sample, transport, storage, and analytical procedures produced acceptable results.

Table E2A. 2001 Canister Laboratory, Trip, and Field Spike Results for Methyl Bromide and 1,3-Dichloropropene for Kern County

Type of Spike	Methyl Bromide Average % Recovery		cis-1,3-Dichloropropene Average % Recovery		trans-1,3-Did Average %	chlorpropene Recovery
Instrument ID	MSD 3	MSD 4	MSD 3	MSD 4	MSD 3	MSD 4
Laboratory	139	117	95	77	83	65
Trip	143	121	101	80	93	70
Field	132	114	90	75	82	60

Source: Operations Planning and Assessment Section, Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Kern County – Summer 2001

Table E2B. 2001 Cartridge Laboratory, Trip, and Field Spike Results for Chloropicrin, MITC. and MIC for Kern County

Type of Spike	Chloropicrin Average % Recovery	MITC Average % Recovery	MIC Average % Recovery
Laboratory	83	45	125
Trip	89	48	110
Field	62	48	100

Source: Operations Planning and Assessment Section, Draft- Ambient Air Monitoring for 1,3-Dichloropropene, Chloropircrin, and Breakdown Products of Metam Sodium in Kern County – Summer 2001

Table E3A. 2001 Canister Laboratory, Trip, and Field Spike Results for Methyl Bromide and 1,3-Dichloropropene for Monterey and Santa Cruz Counties

Type of Spike	Methyl Bromide Average % Recovery		cis-1,3-Dichl Average %		trans-1,3-Dichlorpropene Average % Recovery		
Instrument ID	MSD 3	MSD 4	MSD 3	MSD 4	MSD 3	MSD 4	
Laboratory	152	123	102	95	90	94	
Trip	149	125	101	96	83	91	
Field	156	122	95	90	87	82	

Source: Operations Planning and Assessment Section, Ambient Air Monitoring for Methyl Bromide and 1,3-Dichloropropene in Monterey/Santa Cruz Counties – Fall 2001

Table E3B. 2001 Cartridge Laboratory, Trip, and Field Spike Results for Chloropicrin, MITC, and MIC for Monterey and Santa Cruz Counties

Type of Spike	Chloropicrin Average % Recovery	MITC Average % Recovery	MIC Average % Recovery
Laboratory	82	56	126
Trip	89	55	140
Field	95	55	138

Source: Operations Planning and Assessment Section, Draft- Ambient Air Monitoring for 1,3-Dichloropropene, Chloropircrin, and Breakdown Products of Metam Sodium in Monterey/Santa Cruz Counties – Fall 2001

F. Consumer Products



Consumer products are chemically formulated products used by the public in homes and businesses. These compounds are reported to emit approximately 260 tons per day of smog-forming VOCs. Monitoring VOC levels in consumer products and finding ways to reduce VOC emissions they contain facilitates ARB's effort to reduce smog in the State.

Consumer products are descriptive data sets. Informal data quality objectives have been established and staff ensure the accuracy and precision for data quality are met. Information about the Consumer Products Program is available at http://www.arb.ca.gov/consprod/consprod.htm.

Accuracy: The QAS does not conduct performance audits on the Consumer Product Program at this time. The Special Analysis Section of the Consumer Products Laboratory performs internal quality control activities such as limits of detection, duplicates/replicates, calibrations, control samples, blanks, and trip standards to verify statistical control among analytical methods and ensure valid data are generated.

<u>Precision (lab)</u>: Analytical precision is derived from duplicate analysis performed on a minimum of 10% of the samples. The results from the analyses are compared, and for the sample to be valid, the difference should be less than 3%. Duplicate data that do not meet the criteria may be invalidated. Sample data analyzed on the same date may also be invalidated. Following an investigation of the problem, samples are re-analyzed. Table F1 shows the duplicate data for the 1st quarter of 2001.

Table F1. Duplicate Final %VOC Results for 1st Quarter 2001.

Sample #	Dup 1 %VOC	Dup 2 %VOC	Diff
1	1.0	1.1	0.1
2	19.2	19.9	0.7
3	15.7	15.4	0.3
4	<0.1	<0.1	0.0
5	33.4	34.2	0.8
6	23.9	23.9	0.0
7	44.5	44.7	0.2
8	45.1	44.7	0.4
9	47.3	46.9	0.4
10	42.0	42.3	0.3
11	90.0	86.8	3.2
12	43.0	43.1	0.1
13	63.4	63.4	0.0
14	49.4	50.0	0.6
15	65.0	62.0	3.0
16	81.9	81.9	0.0
17	68.9	68.6	0.3

Note: Diff = ABS (Dup 1 - Dup 2)

The Consumer Product laboratory analyzes known standards (trip standards) to establish control limits and limits of detection, runs system blanks to confirm the system is not contaminated, and conducts yearly multi-point calibrations to assess the instrument linearity. Presently, trip standards should meet the established acceptance criteria of +/-3% difference or have corrective action(s) taken. A sample outside the acceptance criteria prompts staff to investigate quality control activities to verify data generated are valid. Overall, the analytical precision results indicate that the laboratory is providing precise consumer product data. Table F2 represents the trip standard results for the 1st quarter of 2001.

Table F2. Trip Standard Results for 1st Quarter 2001.

				Difference *			
	Total Volatile	Water	Water				
	Material	(KFO)	(GC/TCD)	Acetone	Methanol	Ethanol	% VOC**
Sample #	wt. fraction	wt. fraction	wt. fraction	wt. fraction	wt. fraction	wt. fraction	(Total-Exempt)
1	0.0	0.0	1.0	0.6	0.5	0.6	0.7
2	0.0	1.5	0.4	0.2	0.2	0.6	0.8
3	0.0	1.0	0.4	0.4	0.3	0.0	0.3
4	0.0	1.4	3.7	0.1	0.3	0.3	1.2
5	0.0	0.1	1.4	0.5	0.6	0.2	1.2
6	0.0	0.5	0.8	0.4	0.3	0.1	0.6
7	0.0	4.0	0.9	0.0	0.0	0.4	1.5
8	0.0	N/A	1.0	0.6	0.6	0.2	0.4
9	0.0	N/A	1.4	0.5	0.1	0.5	0.9
10	0.0	N/A	1.1	0.0	0.0	0.4	1.1
11	0.0	N/A	1.0	0.0	0.2	0.2	1.0
12	0.0	N/A	1.5	0.2	0.2	0.7	1.3
13	0.0	N/A	0.9	0.4	0.5	0.0	1.3
14	0.6	N/A	2.0	0.2	0.2	0.6	1.6
15	0.0	N/A	0.1	0.3	0.4	0.1	0.4
16	0.0	N/A	1.6	0.5	0.5	0.9	1.1

N/A = analysis not run

^{*} ABS (Measured - Target)(100)

^{**}ABS (Measured - Target)

G. Meteorology



Meteorological Tower

The ARB monitors meteorological parameters such as wind speed, wind direction, ambient temperature, relative humidity, barometric pressure, and total solar radiation. Real-time meteorological data are generated characterize meteorological processes such as transport and diffusion, and to make air quality forecasts and burnday decisions. The data are also used for control strategy modeling and urban airshed modeling. A State/local meteorology subcommittee of the Air Monitoring Technical Advisory Committee (AMTAC) agreed to define the level of acceptability for meteorological data as those used by the U.S. EPA for the Prevention of Significant Deterioration (PSD) program. The QAS audits to those levels.

The data variability collected by this element of the monitoring program are generally described as meeting or not meeting the PSD requirements. No mandatory corrections are made to the data. However, station operators are notified whether they passed the audit or not. Most operators make the effort to meet the audit standards. The wind speed, wind direction and outside temperature data sets are controlled data sets, and subject to meeting PAMS objectives. Since the inception of the meteorological audit program, the data quality have improved significantly.

Accuracy (field): The accuracy of meteorological sensors are checked by annual performance audits. Table G1 summarizes the 2001 audit results. The average difference (average degree difference with respect to ambient temperature) represents the combined differences from the certified value of all the individual audit points for each sensor. The upper and lower probability limits represent the expected accuracy of 95 percent of all the single sensor's individual percent differences for all audit test levels at a single site. Based on the audit results, ninety-three percent of the instruments audited were found to be operating within the ARB's control limits. operating outside of ARB's control limits resulted in 2,591 days of invalidated meteorological data. Audit results were not used in statistical analysis if the audit was deleted due to an AQDA that resulted in data invalidation. AQDAs do not apply to relative humidity, solar radiation, and vertical wind speed audit results. Information meteorological monitoring available about the program is at http://www.arb.ca.gov/aaqm/met.htm.

Table G1. 2001 Results for Meteorological Sensor Performance Audits Conducted by ARB

	Number				
	of		Avg Diff	Probability Limits	
	Sensors	Number	or Avg		
Sensor	Audited	of AQDAs	% Diff	95%UL	95%LL
Ambient Temp	79	14	0.1	0.7	-0.5
Horiz Wind Speed	105	5	0.0	1.8	-1.8
Relative Humidity	30	NA	0.2	8.5	-8.1
Solar Radiation	23	NA	-2.5	17.1	-22.1
Vert Wind Speed	7	NA	0.0	0.1	-0.1
Wind Direction	96	6	-0.4	3.1	-3.9

NA= Not applicable

Source: Quality Assurance Section, Accuracy Estimates

III. QUALITY CONTROL REPORTS

Quality Control (QC) reports are summaries of the quality control activities conducted by all MLD laboratories to support accurate and precise measurements. These activities include: blanks, duplicates, controls, spiked samples, limits of detection, calibrations, and audit results. Currently, all MLD QC reports are reviewed by the Operations Planning and Assessment Section (OPAS) to verify that good laboratory practices are followed and to identify opportunities for data quality or process improvement. The OPAS Section makes suggestions, where appropriate, to help improve the overall quality and/or effectiveness of the data. In 2001, the Program Evaluation and Standards (PE&S) section reviewed all QC reports. QC reports are prepared quarterly, biannually, or annually, depending upon the program. Table 1 lists the QC reports submitted for review in 2001.

Table 1. Quality Control Reports Submitted to PE&S Section for Review in 2001

Submittal	Title of QC Report	Program (s) Supported
Frequency		
Quarterly	Special Analysis Section, Consumer Products	Consumer Products
Quarterly	Analysis of Motor Vehicle Exhaust	Motor Vehicle Exhaust
Quarterly	Analysis of Motor Vehicle Fuel	Motor Vehicle Exhaust and Fuel Specifications
Quarterly	Inorganic Procedures	Particulate Matter
Quarterly	Organic Procedures	Toxics, Non-Methane Hydrocarbons
Annually	Non-Methane Organic Compounds	Non-Methane Hydrocarbons
Quarterly	Standards Laboratory	All

STANDARDS LABORATORY



The Standards Laboratory performs technical support and certification and verification services of calibration instruments, gases, and devices. Clients include ARB divisions, air districts, and U.S. EPA Region 9 (California, Nevada, Arizona, and Hawaii). Calibrations and certifications are performed for ozone and flow rate transfer standards, certifications of compressed gas cylinders, and verifications of ozone and flow rate primary standards, to ensure that all are traceable to standards of the NIST. A calibration establishes a correction factor to adjust or correct the output of an instrument, a certification establishes traceability of a transfer standard to a NIST-traceable standard, and a verification establishes comparability of a standard to a NIST-traceable standard of equal rank.

The Standards Laboratory also certifies and calibrates on a quarterly basis the instruments used by the ARB's QAS auditors. Table 1 shows the types of services and volume for 2001. Information about the Standards Laboratory and the services that they provide is available at http://www.arb.ca.gov/aaqm/qmosprog/stdslab/stdslab.htm.

Table 1. Standards Laboratory Services Provided for 2001

Service Provided	Number Conducted
Ozone Certifications	36
Ozone Verifications	46
Ozone Calibrations	2
Low Flow Certifications	318
Low Flow Verifications	0
Low Flow Calibrations	2
High Flow Certifications	49
Ambient Gas Cylinders Certified	212
Source Gas Cylinders Certified	251

V. LABORATORY AND FIELD STANDARD OPERATING PROCEDURES

Laboratory and field standard operating procedures (SOPs) are guidance documents for the operation of quality assurance programs used by the ARB, local districts and private industry. The SOPs are intended for field operators and supervisors; laboratory, data processing and engineering personnel; and program managers responsible for implementing, designing, and coordinating air quality monitoring projects. Each



SOP has a specific method that must be followed to produce data-for-record. The SOPs are developed and published to ensure that, regardless of the person performing

the operation, the results will be consistent. Most of the SOPs are available on the Internet at http://www.arb.ca.gov/aaqm/qmosqual/qamanual/qamanual.htm.

VI. SITING EVALUATIONS

To generate accurate and representative data, air monitoring stations should meet specific siting requirements and conditions. It is assumed that the stations met the siting criteria in place at the time initial operation began. As such, non-conformance today is most likely the result of changing regulations, or changes in surrounding conditions and land use. The siting requirements of the ARB's Quality Assurance Manual Volume II; 40 CFR 58, Appendix E; U.S. EPA's Quality Assurance Handbook Volume IV: U.S. EPA's Prevention of Significant Deterioration (PSD); and U.S. EPA's PAMS guidelines, present siting criteria to ensure the collection of accurate and representative data.

The siting criterion for each pollutant varies depending on the pollutant's properties, monitoring objective and intended spatial scale. The U.S. EPA's siting criteria are stated as either "must meet" or "should meet". According to 40 CFR 58, Appendix E, the "must meet" requirements are necessary for high quality data. Any exception from the "must meet" requirements must be formally approved through the Appendix E waiver provision. The "should meet" criteria establish a goal for data consistency.

Siting criteria are requirements for locating and establishing stations and samplers to meet selected monitoring objectives, and to help ensure that the data from each site are collected uniformly. There are four main monitoring objectives: to determine highest concentrations expected to occur in the area covered by the network; to determine representative concentrations in areas of high population density; to determine the impact on ambient pollution levels of significant sources or source categories; and to determine general background concentration levels. Typical siting designations are: micro, middle, neighborhood, and regional. These designations represent the size of the area surrounding the monitoring site which experiences relatively uniform pollutant concentrations. Typical considerations for each of these site designations are, for example, the terrain, climate, population, existing emission sources, and distances from trees and roadways.

Siting evaluations are conducted annually by the QAS. Physical measurements and observations include probe/sensor height above ground level, distance from trees, type of ground cover, residence time, obstructions to air flow, and distance to local sources, are taken to determine compliance with 40 CFR Part 58, Appendix E requirements. If a criteria deficiency is found during a site evaluation, the site operator will be informed and an AQDA may be issued. For siting criteria distances, please refer to Appendix C.

VII. EXAMPLES OF SPECIAL STUDIES

During the course of the year, in-house studies as well as studies abroad are conducted to further the information available about the trends of pollutants and to support regulations to promote the welfare of the public. The following are brief descriptions of some of the special studies that were conducted by MLD.

NIST TRACEABLE ON-SITE CALIBRATION SYSTEM

MLD staff developed a method to provide on-site NIST traceable calibration systems at selected ARB ambient air monitoring stations. Recently, a request to use these systems throughout the ARB's ambient air monitoring network was submitted to the U.S. EPA.

The overall response has been encouraging. The U.S. EPA has tentatively approved the use of the Environics 9100 as a NIST traceable fixed transfer standard in all ARB ambient air monitoring stations. This approval is the culmination of over two years of research, testing, and planning, and will greatly facilitate remote operations of several ambient air monitoring stations in the ARB network.

Certification of the NIST calibrators will be performed on an annual basis. Use of the new systems will greatly improve efficiency by eliminating the need for on-site quarterly equipment calibrations. Using the new systems, analyzer repairs and subsequent calibrations can be performed using the NIST 9100 calibrator in place of a 'carry-in' transfer standard. This will allow staff to perform remote calibrations when practical via the instruments RS232 communications ports.

PORTABLE FUEL CONTAINER REGULATIONS

MLD staff is working to revise regulations designed to limit emissions from portable fuel containers used to fuel off-road equipment. The revised regulations will be presented to the Board in December 2004 for implementation. Major changes to the regulation include a change to a certification program from a consumer products enforcement program and a reference to new ASTM test methods in lieu of near identical test methods adopted by the Board.

SMALL OFF-ROAD ENGINE TANK (SORE) PROJECT

MLD staff is proposing to amend the existing California exhaust emission regulations for small off-road spark-ignition engines to include more stringent standards as well as proposing new regulations to control evaporative emissions from off-road equipment, which utilize engines less than 25 horsepower. This category includes handheld and non-handheld lawn and garden and industrial equipment such as string trimmers, leaf blowers, walk-behind



Honda Mower in Shed

lawn mowers, generators, and lawntractors. The proposed regulations were presented to the Board in September 2003.

CHLOROPICRIN APPLICATION MONITORING

Air monitoring was conducted from October 29 to November 4, 2001 in Monterey County around an application of the fumigant chloropicrin to a field prior to planting strawberries. The monitoring was conducted in support of the Department of Pesticide Regulation's (DPR) air toxics program. The actual pesticide formulation applied was a

50/50 mixture of chloropicrin and methyl bromide. The application was conducted by 'shank' injection into formed 'beds' which were immediately covered with plastic from rolls attached to the back of the application tractor. The process is referred to as a 'bed' fumigation. ARB/MLD staff collected samples for chloropicrin from a number of sites around the field before, during, and for several days following the application. The samples were collected at a distance of approximately 870 feet from the edge of the field. This distance is called the outer buffer zone and is calculated based on DPR regulations that take into account the size of the treated field, the rate of fumigant application, and the product used. DPR staff concurrently collected air samples for methyl bromide. Representatives from the chloropicrin 'Industry' also collected collocated samples for chloropicrin.

CARGO TANK VAPOR RECOVERY CERTIFICATION PROGRAM

The In-Use Vapor Recovery Program Section of MLD in conjunction with the Enforcement Division are working on developing new vapor recovery control measures and strategies for Gasoline Cargo Tanks. Over the next six months, the In Use Vapor Recovery Section will be working on collecting gasoline vapor emission data from cargo tanks and associated equipment. This data will be used to support the current emissions inventories for gasoline cargo tank systems and hoses currently estimated at being 14 – 50 TPD for gasoline vapor emissions. Once this emission data is collected, it will be used to develop a certification program for gasoline cargo tanks and will include equipment specifications and standards, test procedures and control measures to reduce VOC emissions from this source.

PARTICULATE MATTER

MLD staff participated in round 1 of an ongoing program in which participating PM2.5 laboratories analyzed samples from the NIST/National Oceanic Atmospheric Administration (NOAA) Intercomparison Exercise Program for Organic Contaminants in the Marine Environment. The program was used as a model to ensure that PM2.5 organic compounds can be quantitatively compared across the different geographic regions of the country.

PARTICULATE MATTER STANDARD REVIEW AND SAMPLERS COMPARISON STUDY

MLD staff supported the ARB revision of the State Ambient Air Quality Standards for PM and Sulfates, wrote a draft chapter on measurement of particulate matter, and coordinated and completed phase one of a special monitoring study in Bakersfield. The purpose of the study was to evaluate the performance of continuous PM10 and PM2.5 samplers in efforts of verifying a suitable continuous monitor that may be used for attainment designation purposes. Monitoring continued through early 2002.

KING CITY ASBESTOS MONITORING

Staff of MLD's Air Monitoring -North Section completed three phases of monitoring for asbestos in King City. Stationary Source Division (SSD) and the Monterey Bay Unified Air Pollution Control district



(MBUAPCD) requested MLD's assistance to determine the possible source and extent of the presence of asbestos at three schools in King City. Issues of concern to ARB, MBUAPCD, Monterey County Health Department, OEHHA, and the Division of Geology and Mines staff include: 1) whether or not the presence of asbestos is local and confined to the schools (due to removal of asbestos containing materials during modernization activities) or, 2) if the presence of asbestos is a regional issue due to naturally occurring asbestos and, 3) what risk the presence of asbestos poses to the students and the community. The monitoring involved soil sampling and air monitoring under wet and dry conditions to indicate whether or not mitigation procedures are successful in suppressing the asbestos. An assessment of the monitoring reports was presented to the community of King City in 2002.

SB 25 SITE SELECTION AND MONITORING

MLD staff collaborated with district staff and stakeholders groups to select community health monitoring sites as part of Children's Environmental Health Protection Program Senate Bill 25, Escutia 1999) and other community based monitoring programs. Selected criteria pollutants, air toxics, and meteorological parameters were measured using standard methods at the following six stations (Children's Environmental Health Protection monitoring program network): Crockett, Fruitvale (Oakland), Fresno, Boyle Heights (Los Angeles), Wilmington (Long Beach area), and Barrio Logan (San Diego). Monitoring for hexavalent chromium was conducted in Barrio Logan (Barrio Logan II study) to determine community impacts and to support Stationary Source Division's (SSD) revision of the Air Toxic Control Measure (ATCM) specific for hexavalent chromium.

METHOD MODIFICATION TO LOWER Cr(VI) DETECTION LIMIT

MLD staff proposed ways to lower the current method limit of detection (LOD) for analysis of ambient hexavalent chromium (Cr(VI)). Northern Laboratory Branch data showed that over 70% of samples analyzed for Cr(VI) were below the LOD. The feasibility and benefits of doubling sample size to achieve a lower LOD were discussed. Preliminary data generated during July 30 to October 22, 2001, showed that about 45% of the samples reported as zero ng/m3 of Cr(VI) using a single filter extraction were found to have values at or above 0.05 ng/m3 using a composite (double) filter extraction. This showed that extracting composite samples with the same volume as a single filter extraction increased the Cr(VI) detection limit. The study continued through February 30, 2002.

220 VOLT OUTLET POWER SUPPLY FOR AUDITING

Quality Assurance Section (QAS) staff of the MLD completed the first phase of installing 220Volt outlets at select stations in the ambient air monitoring network. Prior to 220Volt outlets in place, power supply for onboard audit equipment was derived from gas powered generators. Implementation of 220Volt outlets provides QAS staff with an alternative to gas powered generators. Field tests results of the 220Volt



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Audit Van Powered by 220Volt Outlet

outlet installed at the Stockton-Mariposa air monitoring station confirm that electric power is a reliable and consistent source of power to conduct successful audits. Electric power is beneficial by providing reductions in noise pollution, reducing costs in gas, and eliminating generator emissions.

PROPOSED TOXICS VOC METHOD CHANGE

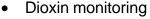
In order to meet the demands of both the toxic air contaminant (TAC) and the Children's Environmental Health Protection Program networks, the Northern Laboratory Branch (NLB) converted the analytical method of volatile organic compound (VOC) analyses to a more sophisticated gas chromatography/mass spectrometry (GC/MS) technique. Prior to the method change, laboratory staff performed VOC analyses using a preconcentration gas chromatograph coupled with both a photoionization detector (PID) and a electron capture detector (ECD). Two main benefits of the GC/MS system include an expanded list of target compounds and lower limits of detection (LODs).

VIII. PROGRAM CONTACTS

Program	Contact	Phone	Email
Gaseous Pollutants	Fred Burriell	(916) 327-0886	fburriel@arb.ca.gov
Particulate Matter	Sam Vogt	(916) 322-8919	svogt@arb.ca.gov
Toxic Air Contaminants	Julie Cooper	(916) 327-0885	jcooper@arb.ca.gov
Non-Methane Hydrocarbons	Julie Cooper	(916) 327-0885	jcooper@arb.ca.gov
Pesticides	Don Fitzell	(916) 322-3892	dfitzell@arb.ca.gov
Consumer Products	Don Fitzell	(916) 322-3892	dfitzell@arb.ca.gov
Meteorology	Fred Burriell	(916) 327-0886	fburriel@arb.ca.gov

IX. UPCOMING ADDITIONS

This report will continue to evolve to include additional QA/QC measurements, new analyses of that information, and summary conclusions about the data meeting our clients' needs for stated objectives. Several elements we expect to include in the next annual issue of this report include:



- Web based audit program development
- Assessment of air monitoring occurring near oil refineries



APPENDIX A

AIR MONITORING NETWORK SURVEY

Quality Assurance Section Monitoring and Laboratory Division





Gaseous Criteria Pollutant Monitoring as of November 9, 2001

Parameter Measured	Ozone	Nitrogen Dioxide	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide*				
Sampling Schedule	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average				
Number of ARB Sites	45	27	25	6	2				
Number of District Sites	145	92	74	74 36					
Number of Sites in Mexico	9	9	9	8	0				
Method Used By ARB	Ultraviolet Photometry	Gas Phase Chemiluminescence	Non-Dispersive Infrared Photometry	Ultraviolet Fluorescence Detector	Thermal Oxidizer with Ultraviolet Fluorescence Detector				
EPA Reference Method	Ultraviolet Photometry	Gas Phase Chemiluminescence	Non-Dispersive Infrared Photometry	Spectrophotometry (Pararosaniline Method)	Not Applicable				
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Aerometric Information Retrieval System (AIRS)								

^{*}Hydrogen Sulfide is only a State criteria pollutant. A Federal standard has not been set.

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Other Monitoring ActivityTab

<u>Acid Deposition | Hydrocarbons | Meteorology</u> <u>PM | TSP and Visibility | Toxic Organic Compounds | Toxic Metals</u>

Particulate Matter Monitoring as of November 9, 2001

		M10) microns)	Size Fraction (0 -2.5 and 2.5		PM2.5		
Parameter Measured	Mass*	Mass* Nitrate, Sulfate, Chloride, Ammonium, Potassium Mass (coarse and fine) Mass (coarse and fine) Al, As, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, K, Mn, Mo, Ni, P, Pb, Rb, S, Sb, Se, Si, Sn, Sr, Ti, U, V, Y, Zn, Zr		Mass (fine)** Speciated			
Sampling Schedule		(24-hr samples) 3 days from Sep to Nov)	Every 6 (24 hr sa	*	Every 3 (Bakersfield and I sites ever	Fresno- First St	
ARB Collection Method		Volume ze Inlet Sampler	Dichotor Selective Size		Mass Sequential & Single Channel		
Sampling Media		crofiber Filter 10 inch	Teflon I 37 n		Teflon Filter 46.2 mm		
Number of Sites Analyzed by the ARB	85* (Includes 14 sites in Mexico)	50 (Includes 13 sites in Mexico)	1	1	38**	0	
Number of ARB Collocated Sites	5	6	1 (Fresno)	1 (Fresno)	9	0	
Additional Sites Analyzed by other Agencies	15 BAAQMD* 34 SCAQMD* 4 SDAPCD* 93 other*	19 SCAQMD	0	0	76**	10***	
ARB Analysis Method	Method 016 Electronic Analytical Balance	Method 007 and Method 023 Ion Chromatography	Method 029 Electronic Microbalance	Method 034 X-Ray Fluorescence	Method 055 Electronic Analytical Balance		
Laboratory Analyst	Yun Pan Scott Randall	Roxana Walker	Yun Pan, Scott Randall Bill Davis Janelle Ayeu		Janelle Ayeung	Betsy Ronsse	
Data Availability		Planning and Technical Suppo U.S. EPA Aerome	rt Division, Air Quality etric Information Retrie		23-4887;		

^{*}These figures include 12 ARB (1 Mexico) and 50 District sites where PM10 mass is monitored continuously (1-hr averages) using TEOM, BAM, or Partisol.

^{**}These figures include 11 ARB and 13 District sites where PM2.5 mass is monitored continuously (1-hr averages) using BAM.

^{***}Analysis performed by EPA laboratory.

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Other Monitoring Activity Tables

Acid Deposition | Gaseous Criteria Pollutants | Hydrocarbons | Meteorology TSP and Visibility | Toxic Organic Compounds | Toxic Metals



TSP and Visibility Monitoring as of November 9, 2001

Parameter Measured	Total Suspended Pa (TSP)	articulates	Coefficient of Haze	Relative Visibility				
Measured	Lead	Sulfate	Particulates	Light Scatter				
Sampling Schedule	Every 6 days (24 hr samples)	1 Every 12 days 4 Every 6 days 2 Every 3 days (24 hr samples)	2-Hour Average	Continuous Hourly Average				
ARB Collection Method	High Volum Total Suspended Partic	Optical Test Tape Sampler	Nephelometer					
Sampling Media	Glass Fiber Fi 8 x 10 incl	Filter Tape	Not Applicable					
Number of Sites Analyzed by the ARB	4 (Includes 1 site in Mexico)	4	23	8				
Number of ARB Collocated Sites	l (Bakersfield)	2 (Bakersfield, San Diego)	0	0				
Additional Sites Analyzed by other Agencies	9 SCAQMD	13 SCAQMD	8	2				
ARB Analysis Method	Method 005 Graphite Furnace Atomic Absorption/ ZEEMAN	Method 033 Ion Chromatography	Light Transmittance Through a Filter Tape	Scattering Coefficient of Light by Suspended Particles				
Laboratory Analyst	Mike Humenny	Roxana Walker	Not Applicable	Not Applicable				
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)							

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Other Monitoring Activity Table

Acid Deposition | Gaseous Criteria Pollutants | Hydrocarbons | Meteorology PM | Toxic Organic Compounds | Toxic Metals



Organic Toxic Air Contaminant Monitoring as of November 9, 2001

		Volatile Organic Compo (VOCs)	unds	Polynuclear Aromatic Hydrocarbons (PAHs)						
Parameter Measured	Aromatic and Halogenated Compounds*	Methyltert-Butyl Ether (MTBE)	Benzo(a)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Dibenz(a,h)anthracene Benzo(g,h,i)perylene Indeno(1,2,3-cd)pyrene							
Sampling Schedule			Every 12 Days (24 hr samples)							
ARB Collection Method	XonTech Gaseous	,	Xontech 920 Toxic Air Contaminant Sampler	High Volume Size Selective Inlet Sampler						
Sampling Media	Polished Stainles	ss Steel Canister	DNPH-Coated Silica Cartridges	Quartz Microfiber Filter 8 X 10 inch						
Number of Sites Analyzed by the ARB	23 (2 in M		23	17						
Number of ARB Collocated Sites	4 (Bakersfield, San Francis	co, San Jose, Rubidoux)	2 (Bakersfield, Stockton)	2						
Additional Sites Analyzed by other Agencies	18 BAA	AQMD	0	0						
ARB Ana;ysis Method	Method 058 Cryogenic Trap Preconcentration Capillary GC/MS Method 050 Cryogenic Trap Preconcentration Capillary GC/PID		Method 022 High-Performance Liquid Chromatography/ Ultraviolet Detector	Method 028 High-Performance Liquid Chromatography/ Fluorescence Detector						
Laboratory Analyst	Ferry Niyati, Pam Gupta Ben Chang, Nati Lapurga	Lynn Yeung Cindy Chain	Paul Chima Dave Hartman	Dave Hartman						
Data Availability		Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)								

^{*} Dichloromethane, trichoromethane, tetrachloromethane, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, bezene, toluene, styrene, 1, 2-dichlorobenzene, 1, 4-dichlorobenzene, o-xylene, m/p xylene, ethylbenzene, and 1,3-butadiene

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Other Monitoring Activity Tables

Acid Deposition | Gaseous Criteria Pollutants | Hydrocarbons | Meteorology PM | TSP and Visibility | Toxic Metals

Toxic Metals Monitoring as of November 9, 2001

		Toxic Metals						
Parameter Measured	Al, As, Ba, Br, Ca, Cl, Co, CR, Cu, Fe, Hg, K, Mn, Mo, Ni, p, Pb, Rb, S, Sb, Se, Si, Sn, Ti, U, V, Y, Zn, Zr	Chromium VI						
Sampling Schedule		Every 12 Days (24 hr samples)						
ARB Collection Method	Toxic	Xontech 920 Toxic Air Contaminant Sampler						
Sampling Media	Teflon Filter 37 mm	DNPH-Coated Silica Cartridges						
Number of Sites /Analyzed by the ARB	23	23						
Number of Collocated Sites	2 (Bakersfield, Stockton)	2 (Bakersfield, Stockton)						
Additional Sites Analyzed by other Agencies	0	0						
ARB Analysis Method	Method 034 X-Ray Fluorescence	Method 022 High-Performance Liquid Chromatography/Ultraviolet Detector						
Laboratory Analyst	Bill Davis Donald Taylor							
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 323-4887; U.S. EPA Aerometric Information Retrieval System (AIRS)							

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Other Monitoring Activity Tables

Acid Deposition | Gaseous Criteria Pollutants | Hydrocarbons | Meteorology PM | TSP and Visibility | Toxic Organic Compounds

Hydrocarbon Monitoring as of November 9, 2001

Parameter	Non-Methane Hydrocar	bon Compound (NMHC)	Continuous	Carbonyl Compounds				
Measured	Total NMHC Speciated NMHC (69 species, C2 through C12)		Non-Methane Hydrocarbons	Acetone Formaldehyde Acetaldehyde				
Sampling Schedule	Every 3 days, July through (3-hr s	September plus episodes amples)	Continuous Hourly Average	3-hr sampler				
ARB Collection Method	XonTech 910A C with XonTech 9	Gaseous Sampler 112 Multisampler	Thermal Environmental (TECO) 55C Hydrocarbon Analyzer	Xontech 925 or other Carbonyl Samplers				
Sampling Media	Polished Stainle	ss Steel Canister	Not Applicable	DNPH-Coated Silica Gel Cartridges				
Number of Sites Analyzed by the ARB	2 (High Ozo	ene Areas)	3	2				
Number of ARB Collocated Sites		1	0	0				
Additional Sites Analyzed by other Agencies	7 SCAQMD (include 4 San Diego (6 San Joaquin 7 Ventura Co 1 Santa Bar	County APCD Valley APCD ounty APCD	16	4 SCAQMD 2 San Diego County APCD 2 San Joaquin Valley APCD 1 Ventura County APCD 1 Santa Barbara APCD				
ARB Analysis Method	Method 024 Cryofocusing Direct GC/FID Method 032 Cryfocusing GC/FID		Flame Ionization Detector	Method 022 High-Performance Liquid Chromatography/Ultraviolet Detector				
Laboratory Analyst	Sean Roy Sean Roy, Barry Taylor		Not Applicable	Paul Chima				
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Aerometric Information Retrieval System (AIRS)							

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Other Monitoring Activity Tables

<u>Acid Deposition | Gaseous Criteria Pollutants | Meteorology</u>

<u>PM | TSP and Visibility | Toxic Organic Compounds | Toxic Metals</u>

Meteorological Monitoring as of November 9, 2001

Parameter Measured	Wind Speed	Wind Direction	Ambient Temperature Relative Humidity		Atmospheric Pressure	Solar Radiation			
Sampling Schedule	Continuous Hourly Average	Continuous Hourly Average	Continuous Hourly Average Continuous Hourly Average		Continuous Hourly Average	Continuous Hourly Average			
Number of ARB Sites	49	49	49	23	19	10			
Number of District Sites	147*	139	112	56	32	39			
Number of Mexico Sites	9	9	9	0	0	0			
Method Used By ARB	Propeller or Cup Anemometer	Wind Vane Potentiometer	Aspirated Thermocouple or Thermistor	Thin Film Capacitor	Not Applicable	Thermopile or Pyranometer			
Data Availability	Planning and Technical Support Division, Air Quality Data Branch, (916) 322-6076; U.S. EPA Aerometric Information Retrieval System (AIRS)								

^{*} Includes 8 vertical wind speed sensors.

 ${\it Michael Miguel, Program \, Contact - } \underline{{\it mmiguel@arb.ca.gov}}$

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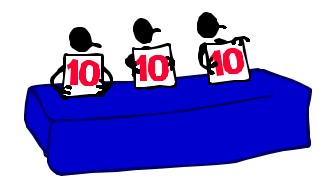
Other Monitoring Activity Tables

Acid Deposition | Gaseous Criteria Pollutants | Hydrocarbons
PM | TSP and Visibility | Toxic Organic Compounds | Toxic Metals

APPENDIX B

2001 DISTRICT USABLE DATA ANALYSIS

Quality Assurance Section Monitoring and Laboratory Division



Precision Data Analysis By District For Usable Data – 2001

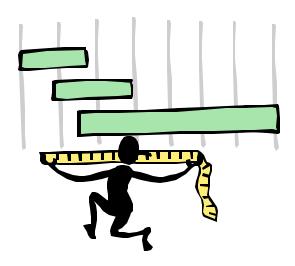
	C	Criteria Pollutants (%)				Particulate Samplers (%)						
District	СО	NO ₂	O ₃	SO ₂	H ₂ S	PM2.5	PM10	PM10 Partisol	Dichot	TEOM	BAM	TSP
Antelope Valley APCD	100	100	100							0		
Bay Area AQMD	100	100	100	99		52	0					
California ARB	93	89	90	100		88	87		48	71		
Environmental Monitoring Company			100									
Glenn County APCD			100									
Great Basin Unified APCD	0					35		82		60		
Imperial County APCD	65	100	69		0							
Lake County APCD			69		96							
Mendocino County APCD	100	100	100			0						
Mojave Desert AQMD	100	100	100	100	100	78				0		
Monterey Bay Unified APCD	100	99	100	100		0						
National Park Service (NPS)			88									
Northern Sierra AQMD			88			71				0		
Northern Sonoma County APCD			100									
Placer County APCD			0									
RMESI (previously known as XonTech, Inc.)				75			64					
Sacramento Metropolitan AQMD	87	88	90	87		37	37			81		
San Diego County APCD	98	97	98	99		78	83					
San Joaquin Valley Unified APCD	98	98	97				40					
San Luis Obispo County APCD	100	94	92	96		93				69		
Santa Barbara County APCD	100	98	100	100	100		98					
SEMARNAT (Mexico – Tracer Technologies)	0	0	0	0						0		
Shasta County APCD			96									
Siskiyou County APCD			74									
South Coast AQMD	96	92	95	93		87	59					
Tehama County APCD			12									
Ventura County APCD	100	99	100	100		58	87					
Yolo-Solano APCD			62									

Note: ARB's goal for usable data is 85%. Precision checks are not required for Kern, Modoc, North Coast, Butte, and Lassen counties for PM2.5 and PM10 (also applies to Coso and EMC companies).

APPENDIX C

SITING CRITERIA DISTANCES

Quality Assurance Section Monitoring and Laboratory Division



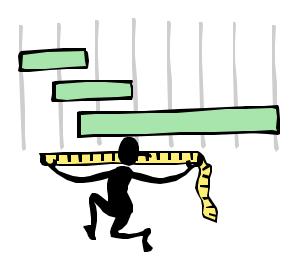
Siting Criteria Distances

0			Charita	Hoight	Dietance	Distance	Distance	
	Height above ground	ve ground	between	above	from	from tree	from walls,	Airflow
Instrument	Micro	Other	samplers	obstructions	obstacles	dripline	parapets, etc.	arc
PM10, AISI Nephelometer	2-7m	2-15m	<4>2m,		2 times height of obstacle above inlet	should be 20m, must be 10m if considered an obstruction	2m	270
Dichot, TEOM, PM2.5	2-7m	2-15m	<4>1m,		2 times height of obstacle above inlet	should be 20m, must be 10m if considered an obstruction	2m	270
Lead, TSP	2-7m	2-15m	<4>2mi		2 times height of obstacle above inlet	micro and middle: no trees between sampler and source, neighborhood: should be 20m, must be 10m if considered an obstruction	2m	270
03	3-15m	3-15m		Jm	2 times height of obstacle above inlet	should be 20m, must be 10m if considered an obstruction	1	270, or on side of building 180
000	2 1/2 - 3 1/2m	3-15m		1m	2 times height of obstacle above inlet	micro: must be no trees between sampler and road, others: must be 10m if trees 5m above sampler.	1m	270, or on side of building 180
NO2	3-15m	3-15m		Jm Tm	2 times height of obstacle above inlet	should be 20m, if individual tree >5m above probe, must be 10m from dripline	Jm	270, or on side of building 180
502	3-15m	3-15m		1m	2 times height of obstacle above inlet	should be 20m, must be 10m if considered an obstruction	1m	270, or on side of building 180
H2S	3-15m	3-15m		1m	2 times height of obstacle above inlet	should be 20m, must be 10m if considered an obstruction	1m	270, or on side of building 180
CH4, THC, NMHC, PAMS	3-15m	3-15m	v	1m	2 times height of obstacle above inlet	should be 20m, must be 10m in direction of urban core	E E	270, or on side of building 180
Toxics Gaseous 910, 910A, 920	3-15m	3-15m		2m	2 times height of obstacle above inlet			
Temperature and Relative Humidity	1.25-2m	1.25-2m			4 times height of obstacle above sensor	~	4.5m	
Wind Speed and Direction	2.5				1.5 times height of obstacle above sensor	2 tower widths from tower side, 1 tower width from tower top		
Solar Radiation								9007 100

APPENDIX D

ARB's INSTRUMENT CONTROL LIMITS

Quality Assurance Section Monitoring and Laboratory Division



Instrument/Sensor Control Limits

ARB's Control and Warning Limits

Limits		Instrument
Control ±15%	Warning ±10%	All Gaseous Criteria and Non-Criteria Analyzers
<u>+</u> 15%	<u>+</u> 10%	Total Suspended Particulate (TSP) Samplers
<u>+</u> 10%	<u>+</u> 7%	PM ₁₀ , Dichotomous (Dichot), Lead (Pb), Tapered Element Oscillating Microbalance (TEOM), Toxic Air Contaminant (XonTech 920) Samplers, Beta Attenuated Monitors (BAM), and Carbonyl (XonTech 925) Samplers
<u>+</u> 4% (Flow) <u>+</u> 5% (Design)	None None	PM _{2.5}
<u>+</u> 20%	None	Laboratory Audits (Toxics, PAMS, Motor Vehicle Exhaust, and Total Metals)
Prevention Of Significant	icant Deterioration (PSD) Crit	eria For Meteorological (MET) Sensors
Limits		Sensor
±0.5° Celsius		Ambient Temperature
±7.50mm of Mercury (Hg)		Barometric Pressure
less than or equal to 5° combined accuracy and orientation error		Wind Direction
less than or equal to 0.5m/s		Wind Direction Starting Threshold
±0.25m/s between 0.5 and 5m/s and less than 5% difference above 5m/s		Horizontal Wind Speed
less than or equal to	0.5m/s	Horizontal Wind Speed Starting Threshold
±0.25m/s between 0 less than 5% differer		Vertical Wind Speed
less than or equal to 0.5m/s		Vertical Wind Speed Starting Threshold

References

- 1. <u>Quality Assurance Handbook for Air Pollution Measurement Systems.</u> <u>Volume I. Principles</u>, EPA-600/9-76-005, January 1984.
- 2. Quality Assurance Handbook for Air Pollution Measure Systems. Volume II. Ambient Air Specific Methods, EPA-600/4-77-027a, May 1977.
- 3. State and Local Air Monitoring Network Plan, California Air Resources Board, May 1993.
- 4. <u>Code of Federal Regulations</u>, Title 40, Protection of the Environment, Part 58, Ambient Air Quality Surveillance (July 1992).
- 5. Air Monitoring Quality Assurance Manual. Volume I. Quality Assurance Plan, Monitoring and Laboratory Division, California Air Resources Board, February 1995.
- 6. Strategic Plan, California Air Resources Board, 1997.
- 7. Technical Assistance Document for Analysis of Ozone Precursors (TAD), September 30, 1998.